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WHEAT STRAW PULPING BY ALKALI-OXYGEN PROCESSES

Cooking variables and pulp properties

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Abstract

A study was undertaken to assess the suitability of wheat straw to be pulped by means of the alkali-oxygen cooking process. The effects of some cooking variables, such as oxygen presence, type and amount of alkali, cooking temperature and time, on yield and Kappa number were evaluated.

The alkaline cooking of wheat straw in the presence of oxygen results in increased delignification. This is especially marked when the alkaline agent has a poor delignification capacity (sodium carbonate or bicarbonate). Thus oxygen seems to be very well suited to use in cooking processes with sodium carbonate liquors.

The use of such liquors can bring about a very interesting simplification of the recovery process.

In the second part of the work the influence of oxygen on pulp properties was evaluated as a function of the alkali used and of some cooking variables.

It is shown that the use of oxygen in alkaline cooking results in fibre degradation which affects the strength properties of the unbleached pulps only in the case of caustic soda cooking. The presence of oxygen during carbonate (or bicarbonate) cooking has favourable effects on pulp strength properties. This behaviour can be attributed to the fact that,

in the case of carbonate cooking, the increment of delignification due to oxygen is far superior to that obtained in caustic cooking.

At equal delignification levels, the oxygen-carbonate pulps show better strength properties than the oxygen-caustic pulps. Long cooking times usually result in negative effects on strength properties.

The use of magnesium ions as inhibitors of carbohydrate degradation, had no definite effect on yield, viscosity, or strength properties.

Introduction

It is well known that oxygen in an alkaline medium can be used as a delignifying agent in pulp bleaching, both as a substitute for chlorine, and as a true cooking agent for chemical pulping.

Although it is accepted that molecular oxygen is a specific oxidising agent for lignin, a first immediate drawback to its use is the low solubility in cooking liquors. This causes serious problems of mass transfer in a heterogeneous chemical process such as wood cooking. Even applying very high oxygen pressure, useful mass transfer of the delignifying agent (molecular oxygen) into the fibre walls, where the reaction should take place, is difficult to obtain in wood chip cooking(1).

Thus cooking processes in two or more stages of different types have been considered. These generally involve a first, more or less mild, cooking stage followed by mechanical defibration. The coarse pulp thus obtained is very suitable for a subsequent alkaline cook in the presence of oxygen due to its higher exposed surface(2-6). Lately, instead of wood chips, thermomechanical fibres have been used for alkali-oxygen cooking(7).

In the case of wheat straw, as for other annual plants, but unlike that of wood, the above problem should be much less important, since the plant structure should permit much easier diffusion and penetration of the delignifying agent (molecular oxygen) into the reactive zones of the fibre wall.

Studies on annual plant cooking by the alkali-oxygen process have been carried out at the CTP in France[8] and in Egypt[9].

Due to the shortage of fibrous raw materials in our country (Italy), we have always paid particular attention to wheat straw as a source for paper pulps. Some plants for the manufacture of such chemical pulps are still operating in Italy. They use highly polluting processes (Pomilio), so it is easy to predict their demise in the near future.

So we thought it would be interesting to investigate wheat straw pulping by means of the alkali-oxygen cooking process. This could lead to the possibility of pollution control through spent liquor chemical recovery. The recovery process would be even simpler, compared with a standard alkaline recovery process (no lime kiln and elimination of all operations connected with caustification), if sodium carbonate could be used as alkaline agent instead of caustic soda.

The first part of this investigation regards the importance of some cooking variables on pulp yield and delignification. In the second part the effects of the alkali-oxygen cooking process on pulp properties were evaluated.

Experimental

The process used consisted of an alkaline cook in the presence of oxygen, under pressure in the digester of 785 kPa.

The cook was carried out in a tumbling digester dipped in an electrically heated oil bath. At the end of the cook the pressure was rapidly reduced to zero and the cooked material was discharged. Fibre separation was accomplished by means of a laboratory disintegrator and, when necessary, by defibration in a laboratory disc refiner. In the latter case care was taken that the clearance between the plates was such as to avoid fibre cutting as much as possible.

Yield was determined on unscreened pulp, whereas screened pulp was used for chemical analysis (Kappa number and viscosity) as well as for beating tests (PFI mill according to ATICELCA MC 211-72).

Handsheets were prepared from beaten and unbeaten pulps using the British mould according to ATICELCA MC 217-79.

Pulp drainability (SR number) and physical properties of handsheets were determined, after conditioning at 20°C and 65% R.H., according to ATICELCA suggested methods.

To evaluate fibre degradation, viscosity tests[18] were carried out on chlorite-delignified pulps.

We started with a caustic soda solution as a cooking liquor, but it was considered necessary to extend the investigation to cooking liquors based on sodium carbonate or bicarbonate.

The possibility of using the latter chemicals has been widely proven[10-13] and lately confirmed at the CTP[8] as appropriate to wheat straw pulping.

The initial pressure of oxygen was maintained at 785 kPa in view of the fact that, on the basis of the results obtained at the CTP[8], pressure variation from 490 to 980 kPa does not seem significantly to affect the main pulp properties.

Other constant cooking conditions were:

- -liquor volume to straw mass ratio: 5 to 1
- -time at cooking temperature: 90 min
- -ratio of $MgCO_3$ to o.d. straw: 1.0 g/100 g.

Effect of cooking variables on yield and delignification

The effect on pulp yield and delignification caused by the following cooking variables was examined:

- -presence of oxygen
- -type of alkali used
- -alkali charge
- -cooking temperature
- -cooking time.

1. Presence of oxygen

Table 1 shows the results relative to alkaline cooking with or without oxygen under pressure.

Cook No	Alkali used Type	Alkali used on o.d. straw g/100 g	O_2 Pressure kPa	Cooking conditions Temperature °C	Time at max. temp. h	Final Pressure kPa	Cooking results Spent Liquor pH	Pulp Yield g/100 g	Kappa Number
575 C	NaOH	10	785	125	2	900	8.0	62.8	37.4
594 C			-			200	10.4	61.1	45.9
574 C	NaOH	20	785	145	2	1100	8.2	51.1	11.1
597 C			-			350	11.5	49.6	17.4
582 C	Na_2CO_3	26.5	785	125	2	1200	8.3	60.9	48.7
595 C			-			200	9.1	69.2	87.2
587 C	Na_2CO_3	26.5	785	145	2	1450	8.0	57.2	30.9
612 C			-			300	9.0	70.5	68.3
596 C	$NaHCO_3$	42	785	145	5	2000	8.1	61.6	37.4
592 C			-			850	8.5	68.6	99.6

Table 1
Effect of Oxygen on cooking results

Cooks with caustic soda liquors (either 10 or 20 percent on o.d. straw) were carried out at temperatures of 125°C or 145°C. Cooks with sodium carbonate at 125°C or 145°C and with sodium bicarbonate at 145°C were performed using chemical charges stochiometrically equivalent to 20 percent of sodium hydroxide on o.d. straw.

The figures in Table 1 show that, under otherwise equivalent cooking conditions, oxygen has a considerable effect on cooking results.

As regards delignification, oxygen cooking in caustic medium results in a Kappa number reduction from 46 to 37 (10% NaOH) or from 17.5 to 11 (20% NaOH). The positive effect of oxygen is even more evident when the alkalinity of the cooking medium is due to sodium carbonate or bicarbonate, that is to chemicals which, unlike caustic soda, have intrinsically poor delignifying power. In these cases oxygen's effectiveness as a delignifying agent, is particularly evident: in fact Kappa numbers decrease from 87 to 49, from 68 to 31, and from 100 to 37 respectively.

As for pulp yield, it can be noted that, in the case of caustic soda, oxygen brings about slightly higher yields. Although reported by other investigations[8,9], the significance of this result needs further confirmation. The better yield can be attributed either to more selective delignification or, more likely, to a reprecipitation of dissolved matter onto the fibre as a consequence of the lower final pH values (about 8 compared to 10 or 11) which result from oxygen cooking.

However, in the case of carbonate or bicarbonate cooking, the presence of oxygen causes marked yield losses mostly attributable to the increased delignification.

The lower pH values obtained in oxygen cooking have already been mentioned for caustic soda: although to a lesser extent, this holds for the other cooks as well.

2. Type of alkali

The type of alkali used in oxygen cooking is of great importance. Table 2 shows the results of oxygen cooks where the alkaline agent was either caustic soda, sodium carbonate, or sodium bicarbonate, other cooking conditions being maintained equal.

As for delignification, caustic soda gave the best results, while bicarbonate was the least effective. At 125°C, depending upon cooking time (2 or 5 hours), the following Kappa numbers were respectively obtained:

- 15 and 12 for caustic soda
- 52 and 49 for carbonate
- 84 and 72 for bicarbonate

At 145°C the Kappa number increases from 11 (caustic soda) to 31 (carbonate), and from 22 (carbonate) to 37 (bicarbonate).

Cook	Alkali used		Cooking conditions			Cooking results		
	Type	on o.d. straw	Temperature	Time at max. temp.	Final Pressure	Spent Liquor	Pulp Yield	Kappa Number
No		g/100 g	°C	h	kPa	pH	g/100 g	
579 C	NaOH	20	125	2	750	8.7	53.1	15.1
581 C	Na_2CO_3	26.5			1200	8.7	60.3	51.7
589 C	$NaHCO_3$	42			1500	8.4	67.5	84.1
580 C	NaOH	20	125	5	650	8.4	52.2	12.0
582 C	Na_2CO_3	26.5			1200	8.3	60.9	48.7
590 C	$NaHCO_3$	42			1500	8.4	66.8	71.7
583 C	Na_2CO_3	26.5	125	8	1200	8.0	61.0	41.1
591 C	$NaHCO_3$	42			1500	8.0	67.8	59.4
574 C	NaOH	20	145	2	1100	8.2	51.1	11.1
587 C	Na_2CO_3	26.5			1450	8.0	57.2	30.9
588 C	Na_2CO_3	26.5	145	5	1400	8.1	53.6	21.9
596 C	$NaHCO_3$	42			2000	8.1	61.6	37.4

Table 2

Effect of type of alkali on alkali-oxygen cooking

As regards the effects on pulp yield, the results obtained do not permit comparisons at equal delignification. However the substitution of carbonate for caustic soda, or bicarbonate for carbonate, resulted in higher yields attributable to lower delignifications, thus with no effect on delignification selectivity.

On the contrary, marked differences can be observed as regards delignification rate: caustic soda gives the fastest cooks, while bicarbonate the slowest ones.

3. Alkali charge

In Table 3 the results are shown for alkali-oxygen cooks where the proportion of alkali to o.d. straw, that is to say the concentration of the alkali agent in the cooking liquor, was varied.

Cook	Alkali used		Cooking results			Cooking results	
	Type	on o.d. straw	Temperature	Time at max. temp.	Spent Liquor	Pulp Yield	Kappa Number
No		g/100 g	°C	h	pH	g/100 g	
575 C	NaOH	10	125	2	8.0	62.8	37.4
579 C		20			8.7	53.1	15.1
578 C	NaOH	10	125	6	7.1	62.1	36.4
580 C		20			8.4	52.2	12.0
572 C	NaOH	10	145	2	6.8	56.5	28.9
574 C		20			8.2	51.1	11.1
581 C	Na_2CO_3	26.5	125	2	8.7	60.3	51.7
601 C		40			8.6	60.6	40.0
587 C	Na_2CO_3	26.5	145	2	8.0	57.2	30.9
602 C		40			8.3	56.5	22.4
590 C	$NaHCO_3$	42	125	5	8.4	66.8	71.7
603 C		63			8.3	62.0	65.7

Table 3

Effect of alkali charge on alkali-oxygen cooking

As far as the effect on delignification is concerned, it can be observed that an increase in caustic soda charge from 10 to 20 percent has a very positive effect on delignification: at 125°C cooking temperature the Kappa number drops from 37 to 15 or from 36 to 12, depending on cooking time, and from 29 to 11 at 145°C. In the case of carbonate or bicarbonate cooks advantageous effects were also obtained, but their extent, especially for bicarbonate, was very much more limited than for caustic soda. It seems clear that the chemical concentration is more important the higher the delignification power of the chemical itself is, independently of the oxygen presence.

Alkali concentration also has an important influence on pulp yield. In the case of caustic liquors an increased concentration results in serious yield losses: the increased delignification does not seem completely to account for these losses. On the contrary, in the case of carbonate or bicarbonate cooks, the yield losses are very limited in accordance with the lower increases in delignification. The lower effectiveness of alkali charge for the latter chemicals is thus confirmed.

4 Cooking temperature

Table 4 presents the results of cooks carried out at two different temperatures for the three alkaline agents considered.

Cook No.	Alkali used: Type	Alkali used: on o.d. straw g/100 g	Cooking conditions: Temperature °C	Cooking conditions: Time at max. temp. h	Cooking results: Spent Liquor pH	Cooking results: Pulp Yield g/100 g	Cooking results: Kappa Number
575 C	NaOH	10	125	2	8.0	62.8	37.4
572 C			145		6.8	56.5	28.9
579 C	NaOH	20	125	2	8.7	53.1	15.1
574 C			145		8.2	51.1	11.1
581 C	Na_2CO_3	26.5	125	2	8.7	60.3	51.7
587 C			145		8.0	57.2	30.9
582 C	Na_2CO_3	26.5	125	5	8.3	60.9	48.7
588 C			145		8.1	53.6	21.9
601 C	Na_2CO_3	40	125	2	8.6	60.6	40.0
602 C			145		8.3	56.5	22.4
590 C	$NaHCO_3$	42	125	5	8.4	66.8	71.7
596 C			145		8.1	61.6	37.4

Table 4
Effect of temperature on alkali-oxygen cooking

It can be easily shown that the use of higher cooking temperatures notably improves delignification. The best results were obtained for carbonate or bicarbonate liquors: a temperature increase from 125°C to 145°C brings about a Kappa number decrease of 20 points in the former case and of 35 points in the latter. For caustic soda the increase in delignification is much more limited: in this case the alkaline agent has such strong delignifying power itself that the margin of action by oxygen is somewhat restricted (e.g., cook N. 579C: 20% NaOH and Kappa number = 15).

As was found before there is a general decrease of yield as cooking temperature is increased: however the existence of a direct relationship between yield decrease and delignification increase needs to be confirmed.

5 Cooking time

Table 5 shows the results of the oxygen cooks aimed at evaluating the effect of cooking time for the three alkaline agents.

Cook	Alkali used		Cooking conditions		Cooking results		
	Type	on o.d. straw	Temperature	Time at max. temp.	Spent Liquor	Pulp Yield	Kappa Number
No		g/100 g	°C	h	pH	g/100 g	
575 C	NaOH	10	125	2	8.0	62.8	37.6
578 C				6	7.1	62.1	36.4
579 C	NaOH	20	125	2	8.7	53.1	15.1
580 C				6	8.4	52.2	12.0
581 C	Na_2CO_3	26.5	125	2	8.7	60.3	51.7
582 C				5	8.3	60.9	48.7
583 C				8	8.0	61.0	41.1
587 C	Na_2CO_3	26.5	145	2	8.0	57.2	30.9
588 C				5	8.1	53.6	21.9
589 C				2	8.4	67.5	84.1
590 C	$NaHCO_3$	42.0	125	5	8.4	66.8	71.7
591 C				8	8.0	67.8	59.4

Table 5

Effect of time at maximum temperature on alkali-oxygen cooking

It can be noted that the extension of cooking time from 2 to 6 hours (caustic soda) or from 2 to 8 hours (carbonate or bicarbonate) does not result in significant yield losses, with the exception of a carbonate cook at 145°C (cook No. 588 C.).

As regards delignification, the use of longer cooks does not seem to be effective in the case of pulps already well delignified (caustic soda), whereas positive effects can be observed for carbonate and especially for bicarbonate.

6. Conclusions

Our experiments have ascertained that the presence of oxygen in alkaline cooking of wheat straw generally results in a higher delignification of the pulps obtained. Oxygen is especially effective when the alkaline agent used has in itself a poor delignification power (sodium carbonate or bicarbonate). Pulp yield does not seem particularly affected by the presence of oxygen: significant losses, as compared with identical cooks without oxygen, were experienced only in cases where very large gains of delignification were obtained. In the case of cooking liquor with a strong delignification power (caustic soda) yield variations did not appear significant.

As for the cooking variables it was found that:

- the type of alkali used plays a major role as regards delignification and, as expected, caustic soda is much more effective than the other chemical agents used;

- the alkali charge (alkali concentration) is important for both delignification and yield: cooking with caustic soda is sensitive to this variable to a much greater extent than carbonate or bicarbonate;

- an increase of cooking temperature brings about higher delignification, which is especially evident for carbonate or bicarbonate cooking;

- longer cooking times have positive delignifying effects in the case of carbonate or bicarbonate cooking.

On the basis of our experiments it can be concluded that the most suitable conditions to be used in alkali-oxygen cooking are:

- in the case of caustic soda: low temperature, short cooking time and high alkali concentration;

- unlike caustic soda, sodium carbonate cooking needs higher temperatures and longer cooking times, as a consequence of the lower delignification power of the chemical agent.

Effect of oxygen cooking on pulp properties

As wheat straw had proved to be very suitable for alkali-oxygen cooking, it was deemed interesting to evaluate the effects on pulp properties which can be brought about by using oxygen, depending on the alkaline medium used and on some cooking variables.

1 Presence of oxygen

Table 6 shows the paper properties of the straw pulps obtained by carbonate (or bicarbonate) oxygen cooking. Table 7 shows the results relative to straw pulps obtained from caustic soda-oxygen cooks.

a . carbonate or bicarbonate cooks (table 6)

Carbonate cooks, with or without oxygen, were carried out at temperatures of 125°C (cook No. 595 C and 582 C) and 145°C (cooks No. 612 and 587 C); for bicarbonate, due to its lower delignification rate, only the highest cooking temperature was used (cooks No. 592 C and 596 C).

TABLE 6 – CARBONATE OR BICARBONATE COOKS: EFFECT OF OXYGEN ON PULP PROPERTIES

Cook No	O_2	Na_2CO_3 on o.d.straw g/100 g	$NaHCO_3$ on o.d.straw g/100 g	Cooking Temp. °C	Time at max. temp. h	Pulp Yield g/100g	Kappa Number	Intrinsic Viscosity dm^3/kg	Drainability SR	Tensile Index kN.m/kg	Stretch %	Burst Index MN.kg	Tear Index $N{\cdot}m^2/kg$	Folding Endurance log cycles	Density kg/m^3
595C	no	26.5	-	125	5	69.2	87.2	-	30	47.5	3.40	2.85	5.70	1.71	680
									50	59.0	4.10	3.70	5.60	2.10	760
582C	yes	26.5	-	125	5	60.9	48.7	-	30	57.5	3.00	3.80	6.00	2.40	705
									50	64.5	3.60	4.25	5.80	2.53	760
612C	no	26.5	-	145	2	70.5	68.3	1050	30	56.0	3.35	3.40	5.15	1.60	680
									50	65.0	3.90	4.25	4.55	2.32	760
587C	yes	26.5	-	145	2	57.2	30.9	650	30	64.0	3.30	4.05	6.00	2.44	740
									50	70.5	3.85	4.65	5.30	2.76	810
592C	no	-	42.0	145	5	68.6	99.6	1075	30	47.0	2.50	2.80	4.95	1.77	655
									50	57.0	3.10	3.50	4.10	2.10	710
596C	yes	-	42.0	145	5	61.6	37.4	555	30	49.0	2.70	2.95	5.20	1.62	680
									50	64.0	3.10	4.20	4.65	1.70	760

Improvements in all strength properties were obtained as a consequence of the presence of oxygen during cooking, particularly in those properties (tensile, burst and folding endurance) which are dependent on fibre bonding. This is also reflected in the higher sheet density. Tearing strength improves as well, but with increments not as pronounced as for the other strength properties.

These better strength properties were obtained despite the fact that the intrinsic viscosity of the pulps (determined after their almost complete delignification) was reduced to roughly half that of the pulps produced without oxygen. The increased delignification is probably responsible for the positive effects on strength properties and is such as to offset the negative impact of carbohydrate degradation.

b. caustic soda cooks (table 7).

In this case the effect of oxygen was evaluated on pulps at delignification levels which were markedly different from each other: thus cooks were carried out with 10% caustic soda at 125°C for 2 hours in one case (cooks No. 594 C and 575 C), and 20% caustic soda at 145°C for 2 hours, in the other one (cooks No. 597 C and 574 C).

It is evident from the results obtained that, unlike what was observed for carbonate or bicarbonate cooks, oxygen generally causes considerable strength losses of the pulps for both delignification levels. This may be attributed to degradation effects suffered by cellulose and hemicellulose during the alkali-oxygen treatment, as is indicated by the relative intrinsic viscosities. However, this would be in disagreement with the results described above for carbonate or bicarbonate cooks. Here too we encounter pulp degradation effects, the extent of which was similar to that seen in caustic soda pulps, but with the difference that they were not accompanied by pulp strength losses.

TABLE 7 - CAUSTIC SODA COOKS: EFFECT OF OXYGEN ON PULP PROPERTIES

Cook No	O_2	NaOH on o.d. straw g/100 g	Cooking Temp. °C	Pulp Yield g/100g	Kappa Number	Intrinsic Viscosity dm^3/kg	Drainability SR	Tensile Index kN•m/kg	Stretch %	Burst Index MN/kg	Tear Index $N•m^2/kg$	Folding Endurance log cycles	Density kg/m^3
594C	no	10	125	61.1	45.9	1290	30	68.0	4.00	4.40	5.85	2.52	760
							50	77.5	4.50	5.30	5.00	2.96	830
575C	yes	10	125	62.8	37.4	615	30	49.0	3.15	2.95	4.75	1.78	730
							50	59.5	3.50	3.85	4.50	2.20	800
597C	no	20	145	49.6	17.4	1170	30	81.5	4.00	5.25	5.00	2.70	810
							50	81.5	4.10	6.05	4.70	2.76	855
574C	yes	20	145	51.1	11.1	605	30	54.0	3.50	3.45	5.50	1.72	770
							50	65.0	3.75	4.45	4.65	2.40	870

For all cooks: time at cooking temperature = 2 hours

This discrepancy can be explained by the fact that, in the case of a carbonate or bicarbonate cook the delignification increment due to oxygen is far superior to that obtained in the caustic soda cook. As already said, the positive effect that the higher delignification of carbonate (or bicarbonate) pulps has on their strength properties, may be such as to overcome the negative impact of carbohydrate degradation.

2. Effect of the type of alkali

Since the amount of residual lignin in the pulp can affect, to a greater or lesser extent, the strength properties of the unbleached pulps, the effect that the type of alkali used has on such properties was evaluated by comparing pulps at delignification levels that were as similar as possible.

Thus comparisons were made between pulps at Kappa numbers of approximately 20 - 60 as a function of the alkaline cooking agents (Table 8).

Examining the results obtained for the pulps at Kappa number of about 20 (cook No. 579 C: caustic soda, and No. 588 C: carbonate) it can be observed that the carbonate pulp had slightly better properties than the caustic soda pulp. This behaviour was even more marked in the case of the pulps at about 30 Kappa number (cook No. 572 C: caustic soda, and No. 587 C: carbonate).

On the whole, the results obtained show that the use of sodium carbonate as a alkaline agent in oxygen cooking, did not impair the strength properties of the pulps: compared with oxygen-caustic soda pulps it provided a positive improvement. The use of bicarbonate, in the delignification range considered, gave results more or less equivalent to those of carbonate.

TABLE 8 - ALKALI-OXYGEN STRAW PULPS AT EQUAL DELIGNIFICATION: EFFECT OF THE ALKALINE COOKING AGENT ON PULP PROPERTIES

Cook No	Cooking agent Type	Cooking agent on o.d. straw g/100 g	Cooking Temp. °C	Time at max. temp. h	Pulp Yield g/100g	Kappa Number	Drainability SR	Tensile Index kN•m/kg	Stretch %	Burst Index MN/kg	Tear Index $N \cdot m^2/kg$	Folding Endurance log cycles	Density kg/m^3
579C	NaOH	20	125	2	53.1	15.1	30	47.0	2.40	2.75	4.65	1.77	735
							50	61.0	3.30	3.95	4.15	2.38	870
588C	Na_2CO_3	26.5	145	5	53.6	21.9	30	55.0	3.05	3.30	5.15	1.88	715
							50	64.5	3.55	4.00	4.35	2.63	785
572C	NaOH	10	145	2	56.5	28.9	30	51.5	2.75	3.55	5.05	1.71	760
							50	66.5	3.40	4.35	4.80	2.38	835
587C	Na_2CO_3	26.5	145	2	57.2	30.9	30	64.0	3.30	4.05	6.00	2.44	740
							50	70.5	3.85	4.65	5.30	2.76	810
575C	NaOH	10	125	2	62.8	37.4	30	49.0	3.15	2.95	4.75	1.78	730
							50	59.5	3.50	3.85	4.50	2.20	800
583C	Na_2CO_3	26.5	125	8	61.0	41.1	30	62.5	2.50	3.90	5.15	2.14	730
							50	68.0	3.10	4.65	4.90	2.52	810
596C	$NaHCO_3$	42	145	5	61.6	37.4	30	48.5	2.70	2.95	5.20	1.62	680
							50	64.0	3.10	4.20	4.65	1.70	760
581C	Na_2CO_3	26.5	125	2	60.3	51.7	30	36.5	2.35	2.25	4.20	1.13	620
							50	47.0	2.95	3.00	3.85	1.45	685
591C	$NaHCO_3$	42	125	8	67.8	59.4	30	41.0	2.75	2.95	4.10	1.40	665
							50	49.0	3.30	3.80	3.45	1.75	740

TABLE 9 - CAUSTIC SODA-OXYGEN STRAW PULPS: EFFECT OF COOKING TIME ON PULP PROPERTIES

Cook No	NaOH on o.d. straw g/100 g	Time at max. temp. h	Pulp Yield g/100g	Kappa Number	Drainability SR	Tensile Index kN•m/kg	Stretch %	Burst Index MN/kg	Tear Index $N•m^2/kg$	Folding Endurance log cycles	Density kg/m^3
575 C	10	2	62.8	37.4	30	49.0	3.15	2.95	4.75	1.78	730
					50	59.5	3.50	3.85	4.50	2.20	800
578 C	10	6	62.1	36.4	30	29.5	2.35	1.70	4.75	0.94	675
					50	41.5	3.25	2.60	4.25	1.31	750
579 C	20	2	53.1	15.1	30	47.0	2.40	2.75	4.65	1.77	735
					50	61.0	3.30	3.95	4.15	2.38	870
580 C	20	6	52.2	12.0	30	35.5	2.60	1.95	4.15	1.16	680
					50	46.0	3.20	2.95	3.50	1.56	780

For all cooks: cooking temperature = 125°C

3. Effect of cooking time

Tables 9, 10 and 11 show the physical characteristics of the alkali-oxygen pulps obtained at increasing cooking times for the three alkaline agents used.

In the case of caustic soda, we evaluated the effect on pulp properties due to a cooking time extension from 2 to 6 hours at 125°C with either 10% (cooks No. 575 C and 578 C) or 20% (cooks No. 579 C and 580 C) chemical on o.d. straw. It can be seen that, as a result, the pulps obtained show serious strength losses and the sheet is bulkier.

As a result of longer cooking times in carbonate cooking (26.5% Na_2CO_3 at 125°C or 145°C) (Table 10) pulps were obtained which gave denser and stronger sheets when cooking at 125°C, but bulkier and weaker sheets when cooking at 145°C.

Prolonging the duration of bicarbonate cooking (Table 11) resulted in the production of pulps with strength properties that were better when the cook was prolonged from 2 to 5 hours, but which returned to the original values after 8 hours cooking.

On the whole the extension of cooking time is not a good way of obtaining better strength properties, except in a few cases: it being thus necessary to use short cooking times, high cooking temperatures become absolutely essential.

4. Effect of use of magnesium carbonate

It is well known that alkaline treatment in the presence of oxygen brings about serious degradation of fibre carbohydrates which can affect the strength properties of the pulps. It was found that this type of carbohydrate degradation can be inhibited by the addition of magnesium compounds(14,15) or iodides(16,17). We then tried to evaluate the eventual effects that the addition of magnesium ions to the cooking liquor can bring about on cooking results and relative pulp properties.

TABLE 10 - CARBONATE-OXYGEN STRAW PULPS: EFFECT OF COOKING TIME ON PULP PROPERTIES

Cook No	Cooking Temperature °C	Time at max. temp. h	Pulp Yield g/100 g	Kappa Number	Drainability SR	Tensile Index kN•m/kg	Stretch %	Burst Index MN/kg	Tear Index $N•m^2/kg$	Folding Endurance log cycles	Density kg/m^3
581 C	125	2	60.3	51.7	30	36.5	2.35	2.25	4.20	1.13	620
					50	47.0	2.95	3.00	3.85	1.45	685
582 C	125	5	60.9	48.7	30	57.5	3.00	3.80	6.00	2.40	705
					50	64.5	3.60	4.25	5.80	2.53	760
583 C	125	8	61.0	41.1	30	62.5	2.50	3.90	5.15	2.14	730
					50	68.0	3.10	4.65	4.90	2.52	810
587 C	145	2	57.2	30.9	30	64.0	3.30	4.00	6.00	2.44	740
					50	70.5	3.85	4.65	5.30	2.76	810
588 C	145	5	53.6	21.9	30	55.0	3.05	3.30	5.15	1.88	715
					50	64.5	3.55	4.00	4.35	2.63	785

For all cooks:
- Na_2CO_3 on o.d. straw = 26.5 g/100 g

TABLE 11 - BICARBONATE-OXYGEN STRAW PULPS: EFFECT OF COOKING TIME ON PULP PROPERTIES

Cook No	Time at max. temp. h	Pulp Yield g/100g	Kappa Number	Drainability SR	Tensile Index kN•m/kg	Stretch %	Burst Index MN/kg	Tear Index $N \cdot m^2/kg$	Folding Endurance log cycles	Density kg/m^3
589 C	2	67.5	84.1	30	40.0	2.50	2.45	5.15	1.30	600
				50	58.0	3.10	3.75	4.40	2.05	700
590 C	5	66.8	71.7	30	49.0	2.55	3.05	4.80	1.82	655
				50	64.0	3.00	3.70	4.30	2.13	715
591 C	8	67.8	59.4	30	41.0	2.75	2.95	4.10	1.40	665
				50	49.0	3.30	3.80	3.45	1.75	740

For all cooks:
- $NaHCO_3$ on o.d. straw: 42 g/100 g
- cooking temperature: 125°C

Thus cooks were carried out using either 10 or 20% caustic soda on o.d. straw with or without 1% magnesium carbonate. The cooking conditions and pulp property results are reported in Table 12.

Cook No	NaOH on o.d. g/100 g	$MgCO_3$ straw g/100 g	Cooking results: Spent Liquor pH	Pulp Yield g/100 g	Kappa Number	Intrinsic Viscosity dm^3/kg
572 C	10	1	6.8	56.6	28.9	650
569 C	10	-	6.9	52.1	24.9	660
574 C	20	1	8.2	51.1	11.1	615
571 C	20	-	8.4	51.2	9.2	570

For all cooks:

- time at max. temp. : 120 min
- cooking temperature: 145°C

Table 12

Effect of magnesium carbonate on the caustic soda-oxygen cooking of straw

As far as the cooking results are concerned, the addition of magnesium carbonate does not seem to cause significant or particular effects on pulp yield and viscosity. As regards the strength properties, the results obtained do not show sufficiently significant differences and seem to point out the ineffectiveness of magnesium carbonate as an inhibitor of carbohydrate degradation. This is in disagreement with data in the literature on oxygen bleaching. However, the ineffectiveness of magnesium carbonate has already been observed by Landucci and Sanyer when wood cooking with alkali-oxygen, whereas the effectivess of iodides has been emphasised[16].

TABLE 13 - CAUSTIC SODA-OXYGEN STRAW PULPS: EFFECT OF MAGNESIUM CARBONATE ON PULP PROPERTIES

Cook No	NaOH on o.d. straw g/100 g	$MgCO_3$	Drainability SR	Tensile Index kN•m/kg	Stretch %	Burst Index MN/kg	Tear Index $N•m^2/kg$	Folding Endurance log cycles	Density kg/m^3
572 C	10	yes	30	51.5	2.75	3.55	5.05	1.71	760
			50	66.5	3.40	4.35	4.80	2.38	835
569 C	10	no	30	52.0	2.95	3.30	4.85	1.83	750
			50	66.0	3.50	4.25	4.35	2.18	855
575 C	20	yes	30	54.0	3.50	3.45	5.50	1.72	770
			50	65.0	3.75	4.45	4.65	2.40	870
571 C	20	no	30	48.0	3.00	3.10	4.60	1.70	780
			50	66.0	3.30	4.40	4.05	2.32	880

Cooking conditions: see Table 12

Neither do the pulp properties show marked variations, with the exception of a little better tearing strength for the pulps produced with magnesium addition.

Thus on the basis of the results obtained, the presence of magnesium ions in the alkali-oxygen cooking liquor seems unnecessary when cooking a material like wheat straw.

5. Conclusions

The results of our investigations make it possible to draw the following conclusions.

The presence of oxygen in caustic soda cooking of wheat straw gives rise to a notable pulp impairment which can be ascribed to carbohydrate depolymerisation by oxygen in the alkaline medium.

In the case of oxygen-carbonate (or bicarbonate) cooking, pulp strength improvements can be observed especially for properties related to fibre bonding: these improvements are obtained despite a depolymerisation effect on carbohydrates of the same extent as for caustic soda cooking: hence they can be attributed to the increased delignification brought about by the oxygen.

This discrepancy of behaviour between caustic soda and carbonate (or bicarbonate) can be explained by the fact that, in the presence of carbonate, oxygen has the possibility of displaying its delignification potential to a larger extent than in the presence of caustic soda liquors. As a matter of fact caustic soda has in itself such a strong delignification power as to leave only limited scope to the action of oxygen.

It was then observed that carbonate-oxygen cooking gives pulps with strength properties on the whole superior to those of the caustic soda-oxygen pulps at equal delignification.

As regards the effect of cooking time, the results obtained lead to the conclusion that excessively long cooking times result, with a few exceptions, in negative effects on strength properties. Thus the use of short cooking times makes it absolutely necessary to apply higher cooking temperatures to obtain the desired delignification levels.

Finally, as regards the action of magnesium carbonate in cooking, this was found to be ineffective in the protection of the carbohydrates of straw fibres against the depolymerisation effect brought about by oxygen in alkaline medium. Neither pulp yield, viscosity, nor strength properties were positively affected by the addition of magnesium ions in the cooking liquor.

Final Remarks

This investigation has definitely proved the suitability of wheat straw for pulping by alkali-oxygen cooking.

Oxygen is very well suited for use with cooking liquors based on sodium carbonate (or bicarbonate). This was shown by the above-mentioned study at CTP[8] and has been amply confirmed by the results of our investigation.

The possibility of using sodium carbonate as cooking agent seems to be particularly interesting: it can open the way to chemical recovery systems that are much simpler than conventional kraft recovery processes. In fact, to recover spent carbonate liquors, the process can be reduced to the combustion of the liquor, eliminating all operations relative to caustification (precipitation with lime, filtration and washing of calcium carbonate mud, lime regeneration) with substantial savings both in operating and capital costs (elimination of lime kiln and of all the equipment related to caustification). In this regard it would be interesting to evaluate the feasibility of small size plants using less traditional combustion systems (e.g. wet combustion, fluidised beds or pyrolysis).

REFERENCES

1. Cox, L.A., and Worster, U.E., Tappi, **54**(11), P.1890-1892.
2. Kleppe, P.J., Chang, H.M., and Eckert, R.C., Pulp & Paper Mag. of Canada, 1972, **73**(12), T400-404.
3. Worster, U.E., Pudek, M.F., and Harrison, R.E. Pulp & Paper Mag. of Canada, 1971, **72**(12), p.69.
4. Palemius, I., and Hiivista, L., Pulp & Paper Mag. of Canada 1970, **71**(21), T465-472.
5. Chang, H.M., MacKean, W.D., Shirley, R.D., and Seay, S., 25th Tappi Alkaline Pulping Conference, Houston, Tex. 1971.
6. Chang, H.M., MacKean, W.D., Gratzl, J.S., and Lian, C.K., 26th Tappi Alkaline Pulping Conference, Memphis, Tenn., 1972.
7. Marton, R., Brown, A., and Granzow, S., Tappi, 1975, **58**(2), p.64-67.
8. Lachenal, D., de Choudens, C., and Monzie, P., ATIP, 1977, **31**(4), p.131-135.
9. El-Ashmavy, A.E., Fadl, M.H., Saleh, T.M., and El-Meadway, S.A., Tappi, 1977, **60**(6), p.109-111.
10. Abrahamsson, K., and Samuelson, O., Svensk Papperstidning, 1972, **75**(21), p.869-873.
11. Jamieson, A.G., Samuelson, O., and Smedman, L.A., Tappi, 1975, **58**(2), p.68-71.
12. Broden, A., and Samuelson, O., Paperi ja Puu, 1975, **57**(9), p.607.
13. Minor, J.L., and Sayner, N., Tappi, 1975, **58**(3), p.116-119.
14. Robert, A., Rerolle,P., Viallet, A., and Martin-Borret, O., ATIP, 1964, **18(4)**, p.151-166.
15. Robert, A., Viallet, A., Rerolle, P., and Andreolety, J.P., ATIP, 1966, **20**(5), p.207.
16. Landucci, L.L., and Sanyer, N., Tappi, 1974, **57**(10), p.97-100
17. Landucci, L.L., and Sanyer, N., Tappi, 1975, **58**(2), p.60-63
18. Prati, G., and Vecchio, G., Ricerca e Docum. Tess., 1965, **2**(4), p.147.

Transcription of Discussion

Discussion following paper presented by Dr. Ceragioli

Mr. A. de Ruvo

Have you considered the effects of different cooking conditions on the degree of crystallinity or the extent of moisture absorption?

Dr. G.Ceragioli, S.S.C., Italy

No. The aim of our work was merely to establish whether the alkali-oxygen process could be used for pulping wheat straw.

Dr. D.W. Clayton

Do you have any comparisons between the properties of pulps made at the same degrees of delignification with and without oxygen?

Dr. G. Ceragioli

Unfortunately not at present, but the work is in progress. However, for caustic soda pulps such a comparison is given in table 7 of my paper, if due allowance is made for the differences in Kappa number.

Dr. J. Ducom, C.T.P., France.

Have you made any economic feasibility studies of your process, especially with application to small units?

Dr. G. Ceragioli

Not at present.

REFERENCE

1 Storebraten, S. and A.J. Kritvary, 1981: "Easy Beaten Sulphate Pulps at 65% Yield", Norsk Skogindustri, **35**, p.53.